

AD 744821

## Time-Resolved Spectroscopy of a Flash-Initiated $H_2-F_2$ Laser

Prepared by S. N. SUCHARD, R. W. F. GROSS, and J. S. WHITTIER  
Acrodynamics and Propulsion Research Laboratory

72 JUN 30

---

Laboratory Operations  
THE AEROSPACE CORPORATION

---

Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION  
AIR FORCE SYSTEMS COMMAND  
LOS ANGELES AIR FORCE STATION  
Los Angeles, California

APPROVED FOR PUBLIC RELEASE.  
DISTRIBUTION UNLIMITED

DDC 16  
RECEIVED  
JUL 14 1972  
RECEIVED  
B

## LABORATORY OPERATIONS

The Laboratory Operations of The Aerospace Corporation is conducting experimental and theoretical investigations necessary for the evaluation and application of scientific advances to new military concepts and systems. Versatility and flexibility have been developed to a high degree by the laboratory personnel in dealing with the many problems encountered in the nation's rapidly developing space and missile systems. Expertise in the latest scientific developments is vital to the accomplishment of tasks related to these problems. The laboratories that contribute to this research are:

**Aerodynamics and Propulsion Research Laboratory:** Launch and reentry aerodynamics, heat transfer, reentry physics, propulsion, high-temperature chemistry and chemical kinetics, structural mechanics, flight dynamics, atmospheric pollution, and high-power gas lasers.

**Electronics Research Laboratory:** Generation, transmission, detection, and processing of electromagnetic radiation in the terrestrial and space environments, with emphasis on the millimeter-wave, infrared, and visible portions of the spectrum; design and fabrication of antennas, complex optical systems and photolithographic solid-state devices; test and development of practical superconducting detectors and laser devices and technology, including high-power lasers, atmospheric pollution, and biomedical problems.

**Materials Sciences Laboratory:** Development of new materials; metal matrix composites and new forms of carbon; test and evaluation of graphite and ceramics in reentry; spacecraft materials and components in radiation and high-vacuum environments; application of fracture mechanics to stress corrosion and fatigue-induced fractures in structural metals, effect of nature of material surfaces on lubrication, photosensitization, and catalytic reactions, and development of prosthesis devices.

**Plasma Research Laboratory:** Reentry physics and nuclear weapons effects; the interaction of antennas with reentry plasma sheaths, experimentation with thermonuclear plasmas, the generation and propagation of plasma waves in the magnetosphere; chemical reactions of vibrationally excited species in rocket plumes; and high-precision laser ranging.

**Space Physics Laboratory:** Aeronomy, density and composition of the atmosphere at all altitudes; atmospheric reactions and atmospheric optics; pollution of the environment; the sun, earth's resources, meteorological measurements; radiation belts and cosmic rays, and the effects of nuclear explosions, magnetic storms, and solar radiation on the atmosphere.

THE AEROSPACE CORPORATION  
El Segundo, California

|  |  |
|--|--|
| 1. DISTRIBUTION AVAILABILITY CODES<br>DIST.    AVAIL. and/or SPECIAL<br><div style="font-size: 2em; margin-top: 10px;">A</div> | 2. SECTION<br>3. SECTION<br>4. SECTION |
|--|--|

| DOCUMENT CONTROL DATA - R & D<br>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)   |   |   |
|---|---|---|
| 1 ORIGINATING ACTIVITY (Corporate author)<br><br>The Aerospace Corporation<br>El Segundo, California  |   | 2a REPORT SECURITY CLASSIFICATION<br>Unclassified |
|   |   | 2b GROUP  |
| 3. REPORT TITLE<br><br>TIME-RESOLVED SPECTROSCOPY OF A FLASH INITIATED H <sub>2</sub> -F <sub>2</sub> LASER   |   |   |
| 4 DESCRIPTIVE NOTES (Type of report and inclusive dates)  |   |   |
| 5 AUTHOR(S) (First name, middle initial, last name)<br><br>Steven N. Suchard, Rolf W. F. Gross, and James S. Whittier   |   |   |
| 6 REPORT DATE<br>72 JUN 30  | 7a TOTAL NO OF PAGES<br>12  | 7b NO OF REFS<br>15                               |
| 8a CONTRACT OR GRANT NO<br>F04701-71-C-0172   | 9a ORIGINATOR'S REPORT NUMBER(S)<br>TR-0172(2753)-2   |   |
| b PROJECT NO  |   |   |
| c   | 9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report)  |   |
| J   | SAMSO-TR-72-157   |   |
| 10 DISTRIBUTION STATEMENT<br><br>Approved for public release; distribution unlimited  |   |   |
| 11 SUPPLEMENTARY NOTES  | 12 SPONSORING MILITARY ACTIVITY<br>Space and Missile Systems Organization<br>Air Force Systems Command<br>Los Angeles, California |   |
| 13 ABSTRACT<br><br>The time-dependent output spectrum of a helium-diluted H <sub>2</sub> -F <sub>2</sub> chain reaction chemical laser has been observed. Reaction of a 50-Torr mixture with mole ratio H <sub>2</sub> :F <sub>2</sub> :He = 1:1:60 was initiated by flash photolysis of the F <sub>2</sub> . Strong lasing was found from P-branch vibration-rotation transitions of the v - 1+0, 2+1, 3+2, and 4+3 bands of HF. Within some bands, the time sequence of transitions suggests non-Boltzmann distributions of rotational states. No lasing from vibrational levels higher than 4 could be detected. |   |   |

I

UNCLASSIFIED

Security Classification

14.

KEY WORDS

Lasers

Chemical Lasers

Chain-Reaction Lasers

Spectroscopy

Time-Resolved Spectroscopy

Distribution Statement (Continued)

Abstract (Continued)

11-

UNCLASSIFIED

Security Classification

Air Force Report No.  
SAMSO-TR-72-157

Aerospace Report No.  
TR-0172(2753)-2

TIME-RESOLVED SPECTROSCOPY OF A FLASH  
INITIATED  $H_2-F_2$  LASER

Prepared by  
S. N. Suchard, R. W. F. Gross, and J. S. Whittier  
Aerodynamics and Propulsion Research Laboratory

72 JUN 30

Laboratory Operations  
THE AEROSPACE CORPORATION

Prepared for  
SPACE AND MISSILE SYSTEMS ORGANIZATION  
AIR FORCE SYSTEMS COMMAND  
LOS ANGELES AIR FORCE STATION  
Los Angeles, California

Approved for public release;  
distribution unlimited

*III*


## FOREWORD

This work reflects research supported by the Advanced Research Projects Agency of the Department of Defense under U.S. Air Force Space and Missile Systems Organization (SAMSO) Contract F04701-71-C-0172.

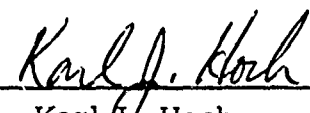
This report, which documents research carried out from November 1970 to January 1971, was submitted 19 August 1971 to Captain Carl J. Hoch, SYAE, for review and approval.

The authors express their appreciation for the interest and support of Drs. W. R. Warren, Jr., T. A. Jacobs, N. Cohen, M. A. Kwok, G. Emanuel, and Major M. Berta and for the technical assistance of R. Uenten, A. Ching, and L. Bergerson.

Approved

  
\_\_\_\_\_  
W. R. Warren, Jr., Director  
Aerodynamics and Propulsion Research  
Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

  
\_\_\_\_\_  
Karl J. Hoch  
Capt., United States Air Force  
Project Officer

TV

## ABSTRACT

The time-dependent output spectrum of a helium-diluted  $\text{H}_2\text{-F}_2$  chain reaction chemical laser has been observed. Reaction of a 50-Torr mixture with mole ratio  $\text{H}_2\text{:F}_2\text{:He} = 1\text{:}1\text{:}60$  was initiated by flash photolysis of the  $\text{F}_2$ . Strong lasing was found from P-branch vibration-rotation transitions of the  $v = 1 \rightarrow 0$ ,  $2 \rightarrow 1$ ,  $3 \rightarrow 2$ , and  $4 \rightarrow 3$  bands of HF. Within some bands, the time sequence of transitions suggests non-Boltzmann distributions of rotational states. No lasing from vibrational levels higher than 4 could be detected.

V

## CONTENTS

|                      |     |
|----------------------|-----|
| FOREWORD . . . . .   | ii  |
| ABSTRACT . . . . .   | iii |
| DISCUSSION . . . . . | 1   |
| REFERENCES . . . . . | 9   |

## FIGURES

|   |   |
|---|---|
| 1. Selected HF Laser Transitions from Flash Photolysis<br>of a 1:1:60 - $H_2:F_2:He$ Mixture . . . . .          | 4 |
| 2. Time-Resolved Spectroscopy of the Observed Laser<br>Transitions of a 1:1:60 - $H_2:F_2:He$ Mixture . . . . . | 7 |

## TABLES

|   |   |
|---|---|
| 1. Measured wavelengths, calculated wavelengths,<br>identification and peak powers of HF laser transitions<br>observed in flash photolysis of $H_2$ and $F_2$ . . . . . | 5 |
|---|---|



## TIME-RESOLVED SPECTROSCOPY OF A FLASH INITIATED $\text{H}_2\text{-F}_2$ LASER

We have spectroscopically investigated the time-dependent output of an HF laser. The HF vibration-rotation inversion was produced by the chain reaction of  $\text{H}_2$  and  $\text{F}_2$  highly diluted with helium. This reaction has chain steps



The reaction was initiated by flash photolysis of  $\text{F}_2$ .

Spectroscopic investigations of HF lasers produced by the  $\text{H}_2\text{-F}_2$  reaction have been reported by Oraevskii<sup>1</sup> and Talrose.<sup>2</sup> They investigated the reaction of undiluted  $\text{H}_2\text{-F}_2$  mixtures initiated by either an electrical pulse discharge or flash photolysis. Recently, Hess<sup>3</sup> reported observations of a photolytically-initiated  $\text{H}_2\text{-F}_2\text{-He}$  laser but presented no spectral information. Our choice of a diluted  $\text{H}_2\text{-F}_2$  system in combination with photolytic initiation was motivated by the expectation that such a system would eventually permit a detailed analysis of the chemical kinetics involved. Such an analysis is in progress.<sup>4</sup> This letter reports preliminary findings justified by notable differences in spectral composition of the laser output compared to Refs. 1 and 2, and the fact that no detailed time-dependent spectroscopy of the  $\text{H}_2\text{-F}_2$  system has been previously reported.

Experiments were performed with continuously flowing mixtures. The apparatus consisted of a quartz laser tube of 12-mm I. D. and 75-cm length fitted with sapphire Brewster windows and placed inside a 100-cm cavity formed by a spherical mirror of 3.10-m radius and either a dielectric flat (sapphire substrate) with 15% transmittance, or a hole-coupling flat of 5-cm diam with a 2-mm-diam hole. Mirror and hole coupler were gold-coated to

a nominal reflectivity of 98%. Helium and fluorine (Matheson, 99%) were premixed in a passivated stainless steel bottle at 5.1 atm. A flow of the  $F_2$ -He mixture was delivered through a regulating valve to a mixer where it was injected through a calibrated sonic orifice into a metered  $H_2$ -He flow. The mixer and 50 cm of tubing connecting it to the laser tube were made from aluminum as a precaution against pre-ignition of the mixture.<sup>5</sup> Gases from the laser tube were exhausted by a 30 l/min mechanical vacuum pump (Kinney) after passing through a carbon trap that protected the pump from unreacted  $F_2$ . Pressures were measured with gauges (Heise) having Cu-Be Bourdon tubes.

The spectrograph was a 1.0-m Czerny-Turner instrument of our own manufacture<sup>6</sup> equipped with a 300-line/mm grating blazed at  $3.0 \mu m$  in first order, used as a monochromator with a resolution of  $\pm 2.5 \text{ cm}^{-1}$ . Radiation was monitored with Au-Ge photoconductive detectors (Raytheon). Total rise-time of detector and oscilloscope was estimated to be 20 nsec.

Any prereaction of the flowing  $H_2$ - $F_2$ -He before flash initiation was detected by monitoring the uv absorption<sup>5</sup> of the  $F_2$ . Radiation from a high-pressure mercury lamp (Osram) was passed through the laser tube and a band filter at  $270 \pm 10 \text{ nm}$  and then detected by a photomultiplier. Use of a differential comparator amplifier (Tektronix Type W) permitted resolution of small changes in the photomultiplier output. After calibration, we were able to infer the  $F_2$  partial pressure to an accuracy of better than 5 %. For these experiments, in admitting the  $H_2$ , we found no loss of  $F_2$  within this accuracy. Thus, we believe there was no significant population of HF in the laser tube before flash initiation.

A xenon flash lamp of 56-cm active length (Kemlite) energized by a 14.7- $\mu F$ /20-kV capacitor served to trigger the reaction. Lamp and laser tube were coupled optically by a 5-cm-diam aluminum foil reflector. We calculate that this arrangement photodissociated about 1% of the  $F_2$  in the illuminated portion of the laser tube.

Figure 1 shows a composite of oscilloscope traces for flash lamp output, total laser output, and some of the stronger laser lines. The observed laser pulse has a duration of 75  $\mu$ sec, which is comparable with those reported by Hess<sup>3</sup> for diluted  $H_2-F_2$  and considerably longer than the Soviet<sup>1,2</sup> results for undiluted  $H_2-F_2$ . The difference in pulse lengths is to be expected because of the temperature control provided by dilution and because much shorter initiation pulses were used for the undiluted experiments.

Table 1 shows wavelengths and peak powers for the observed laser lines along with calculated wavelengths<sup>7</sup> for the transitions with which we have identified our observations. We have found strong lasing from the  $v = 1 \rightarrow 0$ ,  $2 \rightarrow 1$ ,  $3 \rightarrow 2$ , and  $4 \rightarrow 3$  bands and no lasing from  $5 \rightarrow 4$  or  $6 \rightarrow 5$ . This is in contrast to Oraevskii<sup>1</sup> who found strong lasing from  $2 \rightarrow 1$ , weak lasing<sup>8</sup> from  $3 \rightarrow 2$ ,  $4 \rightarrow 3$ ,  $5 \rightarrow 4$  and  $6 \rightarrow 5$ , and no lasing from  $1 \rightarrow 0$ . Talrose<sup>2</sup> carried out only a partial spectroscopic analysis of his laser output. However, he did observe lasing on the  $1 \rightarrow 0$  band.

Among explanations for the absence of  $1 \rightarrow 0$  lines in his results, Oraevskii cites the possible presence of ground state HF in his initial mixtures. We have made observations that tend to reinforce this explanation. On raising the total pressure of the  $H_2:F_2:He = 1:1:60$  mixture to 100 Torr in our apparatus, we find, by uv absorption measurement, that about 10% prereaction has occurred. From this, we infer that the average composition of the gas flowing in the laser tube is then about  $H_2:F_2:HF:He = 0.9:0.9:0.2:60$ . Under these conditions, lasing on the  $1 \rightarrow 0$  band is greatly reduced. At higher pressures, where the extent of prereaction is greater, we found no  $1 \rightarrow 0$  lasing.

Contrary to observations by Oraevskii,<sup>1</sup> we observe strong lasing from  $v = 4 \rightarrow 3$  transitions. Thus, chain branching reactions,<sup>9</sup> which were mentioned by Oraevskii as a  $v = 4$  depopulation mechanism to explain his weak lasing from  $v = 4 \rightarrow 3$ , do not appear to play a significant role under the conditions of our experiment. Talrose<sup>2</sup> came to a similar conclusion.

Recently, Johathan<sup>10</sup> measured the vibrational distribution function for the Reaction (2) at room temperature and found pumping of all levels up to  $v = 6$ . In particular, his results indicate that in the absence of other

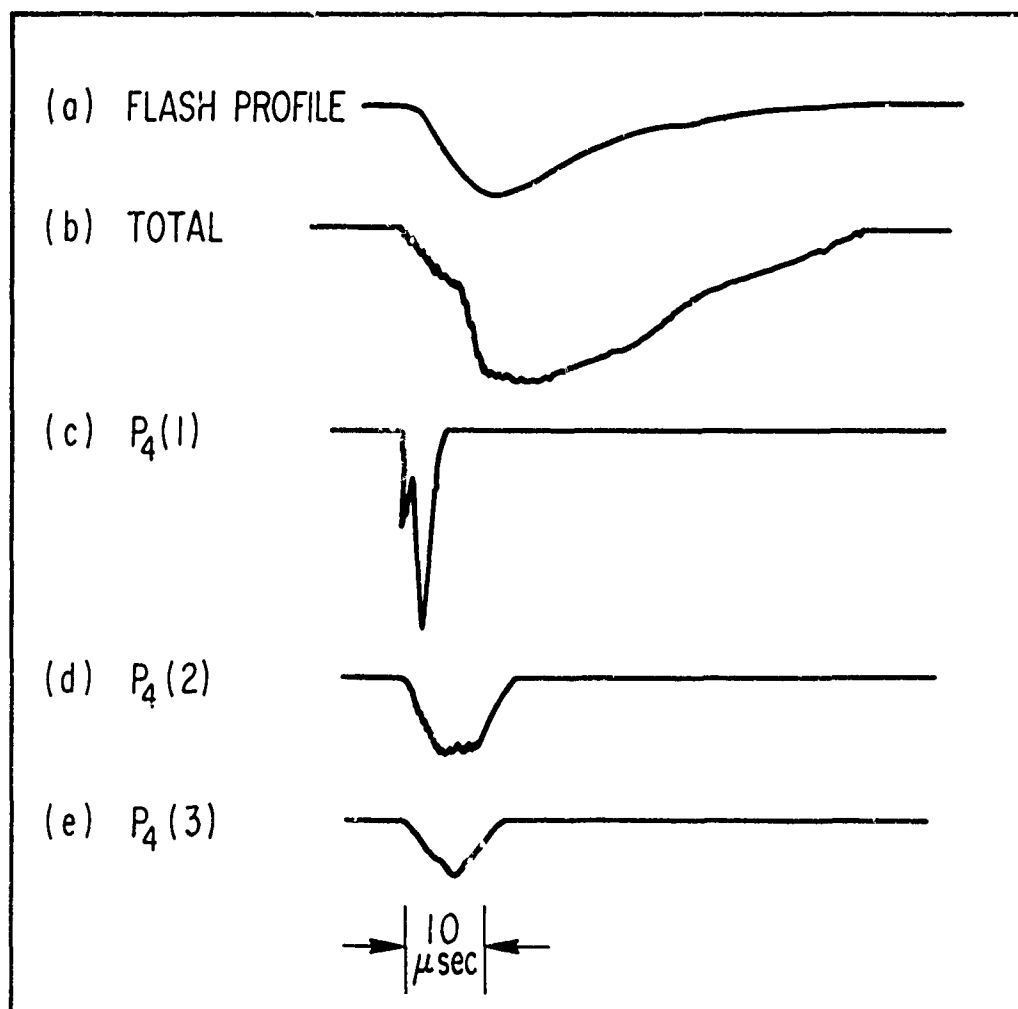


Figure 1. Selected HF Laser Transitions from Flash Photoysis of a 1:1:60 -  $\text{H}_2:\text{F}_2:\text{He}$  Mixture

Total pressure, 50 Torr; flash energy, 1575J. (a) Flash lamp profile, (b) total laser emission, (c - e) individual transitions from the 4th to 3rd vibrational levels.

Table 1. Measured wavelengths, calculated wavelengths, identification, and peak powers of HF laser transitions observed in flash photolysis of  $H_2$  and  $F_2$ .

| Measured <sup>a</sup><br>Wavelength<br>( $\mu m$ ) | Vibrational<br>Band | Identification<br>Transition<br>(J) | Calculated<br>Wavelength<br>( $\mu m$ ) | Peak Power<br>(relative units) |
|--|---------------------|-------------------------------------|---|--------------------------------|
| 2.6069   | 1-0                 | 3                                   | 2.6084                                  | <1                             |
| 2.6386   |                     | 4                                   | 2.6396                                  | <1                             |
| 2.6753   |                     | 5                                   | 2.6726                                  | 40                             |
| 2.7068   |                     | 6                                   | 2.7074                                  | 130                            |
| 2.7424   |                     | 7                                   | 2.7440                                  | 28                             |
| 2.7850   |                     | 8                                   | 2.7826                                  | 107                            |
| 2.6663   | 2-1                 | 1                                   | 2.6668                                  | 6                              |
| 2.6953   |                     | 2                                   | 2.6963                                  | 300                            |
| 2.7298   |                     | 3                                   | 2.7275                                  | 600                            |
| 2.7624   |                     | 4                                   | 2.7604                                  | 300                            |
| 2.7963   |                     | 5                                   | 2.7952                                  | 62                             |
| 2.8326   |                     | 6                                   | 2.8319                                  | 8                              |
| 2.8684   |                     | 7                                   | 2.8705                                  | <1                             |
| 2.7894   | 3-2                 | 1                                   | 2.7902                                  | 165                            |
| 2.8222   |                     | 2                                   | 2.8213                                  | 170                            |
| 2.8551   |                     | 3                                   | 2.8542                                  | 417                            |
| 2.8915   |                     | 4                                   | 2.8890                                  | 379                            |
| 2.9258   |                     | 5                                   | 2.9257                                  | 4                              |
| 2.9648   |                     | 6                                   | 2.9644                                  | 14                             |
| 3.0061   |                     | 7                                   | 3.0052                                  | 2                              |
| 3.0509   | 4-3                 | 8                                   | 3.0482                                  | 8                              |
| 2.9183   |                     | 1                                   | 2.9221                                  | 320                            |
| 2.9555   |                     | 2                                   | 2.9549                                  | 126                            |
| 2.9882   |                     | 3                                   | 2.9896                                  | 60                             |

<sup>a</sup>Estimated accuracy  $\pm 2.5 \text{ cm}^{-1}$

mechanisms this reaction should produce a total inversion for the  $v = 5 \rightarrow 4$  band. Thus, Oraevskii's observation of only weak lasing on  $5 \rightarrow 4$  and our failure to observe lasing at all seems curious.

The time-sequential behavior of the observed transitions is presented in Fig. 2. This diagram has  $V, J$  levels as ordinate and time measured from the onset of the flashlamp as abscissa. The observed duration for each transition is displayed as a horizontal bar along its upper level, with the time of peak intensity marked with a circle. Vertical arrows extend to the appropriate lower levels to facilitate examination of the diagram for cascade phenomena. As has been observed in time-resolved spectroscopy<sup>11-13</sup> of HF lasers driven by Reaction (1),  $P_2(3)$  is the first transition to reach threshold. This transition is unique in that it has two separate intervals of activity. For the most part, the time sequencing of the transitions demonstrates that, as the reaction progresses and heats the reactants, the transition of maximum gain in a specific vibrational band shifts sequentially to higher rotational levels. Appearance of some transitions ahead of their sequential turn signifies the presence of rotational nonequilibrium. Reassuring for theoretical modeling, where rotational equilibrium affords great simplification, is the fact that all but one of the out-of-sequence transitions exhibits relatively weak lasing.

An unusual feature of the data is the observation of  $P_2(1)$ ,  $P_3(1)$ , and  $P_4(1)$  lines. However, these observations may be explainable in terms of the Einstein coefficient for spontaneous emission and the initial rotational level distribution of the vibrationally-excited HF molecules. Observations by Kompa<sup>14</sup> for the  $WF_6/H_2$  and  $WF_6/CH_4$  systems leave open the possibility that the initial rotational distribution of Reaction (1) may be peaked near  $J=0$  or 1. No studies have been done on the initial rotational distribution of Reaction (2). Work done by Meredith<sup>15</sup> shows the Einstein coefficient of spontaneous emission from the P-branch transition  $J=0 \rightarrow J=1$  to be about 50% greater than for the transition  $J=1 \rightarrow J=2$  for all vibrational bands. It is felt that the combined effect of these two phenomena may prove to be the explanation for the observation of the  $P_2(1)$ ,  $P_3(1)$ , and  $P_4(1)$  transitions.

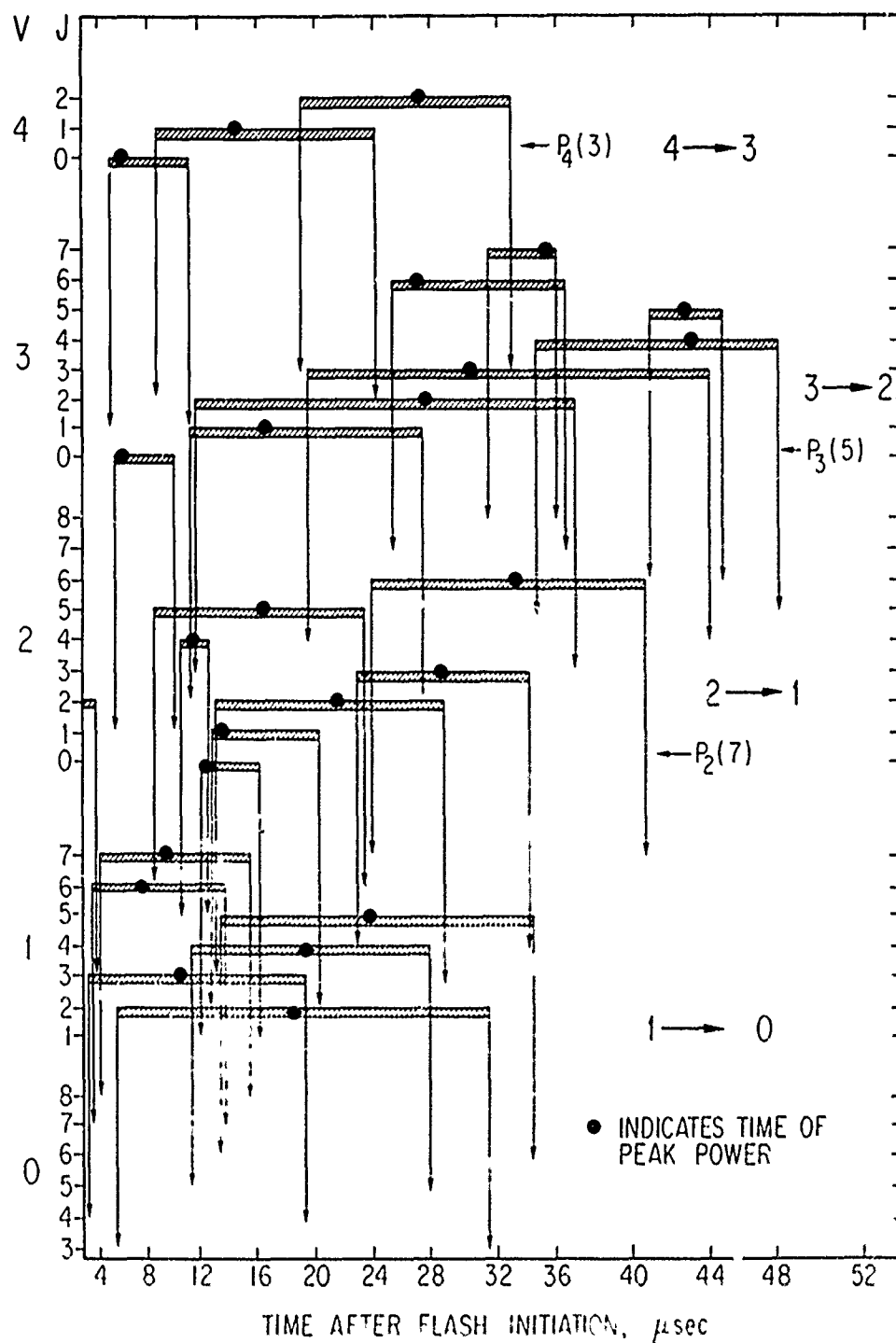


Figure 2. Time-Resolved Spectroscopy of the Observed Laser Transitions of a 1:1:60 -  $\text{H}_2:\text{F}_2:\text{He}$  Mixture

Total pressure c. 50 Torr.

## REFERENCES

1. N. G. Basov, L. V. Kulokov, E. P. Markin, A. I. Nikitin, and A. N. Oraevskii, Zh. Eksperim. i Teor. Fiz., Pis'ma v Redaktsiyu 9, 613 (1969).
2. O. M. Batovskii, G. K. Vasil'ev, E. F. Makarov and V. L. Talrose, Zh. Eksperim. i Teor. Fiz., Pis'ma v Redaktsiyu 9, 341 (1969).
3. L. D. Hess, Appl. Phys. Letters (to be published).
4. G. Emanuel, S. N. Suchard, and J. S. Whittier (unpublished communication).
5. A. V. Grosse and A. D. Kirshenbaum, J. Phys. Soc. 77, 5012 (1955).
6. E. W. Hewitt, J. P. Bott, and T. A. Jacobs, Rev. Sci. Instr. 41, 1416 (1970).
7. D. E. Mann, et al., J. Chem. Phys. 34, 420 (1961).
8. Oraevskii reports finding lasing on these bands only after constructing an optical cavity using dielectric mirrors with reflectivity of 99.8%.
9. G. A. Kapralova, et al., Kinetika i Kataliz 4, 653 (1963).
10. N. Johathan, C. M. Melhar-Smith, and D. Slater, J. Chem. Phys. 53, 4396 (1970).
11. K. L. Kompa, J. H. Parker, and G. C. Pimentel, J. Chem. Phys. 49, 4257 (1968).
12. J. H. Parker and G. C. Pimentel, J. Chem. Phys. 51, 91 (1969).
13. W. H. Green and M. C. Liu, IEEE J. Quantum Electron. 7, 98 (1971).
14. K. L. Kompa, J. Wanner, and P. Gensel, Paper presented at Second Conference on Chemical Molecular Lasers, St. Louis, Mo., May 1969.
15. R. Meredith (private communication).